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16. ABSTRACT

As part of quality assurance performance audits on three U.S. Environmental Protection Agency ambient air monitoring projects, the suppression in the total sulfur response due to carbon dioxide was measured on flame photometric detector (FPD) total sulfur analyzers. Each analyzer was challenged at the 50, 100, and 150 ppb SO_2 level using air containing 0, 360, and 750 ppm CO_2. Four different models of FPD total sulfur analyzers were evaluated. Six or more analyzers were evaluated for each model. Suppression in analyzer response due to CO_2 was observed in all four models at all three SO_2 levels.

At each monitoring project, ambient air is scrubbed and used as the dilution air during a multipoint calibration. Simultaneous measurements of CO_2 in the ambient air and CO_2 in the scrubbed calibration air showed partial and variable removal of CO_2 by the scrubbing system. At EPA monitoring Project No. 1, simultaneous measurements of CO_2 in the ambient air and in the calibration air were performed at 23 monitoring stations. On an average for the total 23 stations, the CO_2 in the calibration air was 328 ppm lower than that in the ambient air being sampled at the stations. Concern exists that some monitoring networks may be calibrated with calibration air containing low CO_2 and then returned to service to analyze ambient air containing a significantly higher CO_2 concentration.

By proper treatment of the calibration air, the CO_2 suppression on FPD total sulfur response may be minimized. An activated charcoal scrubber is recommended for proper treatment of the calibration air.

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Suppression Effect of CO_2 on FPD Total Sulfur Air Analyzers and Recommended Corrective Action

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ABSTRACT

As part of quality assurance performance audits on three U.S. Environmental Protection Agency ambient air monitoring projects, the suppression in the total sulfur response due to carbon dioxide was measured on flame photometric detector (FPD) total sulfur analyzers. Each analyzer was challenged at the 50, 100, and 150 ppb SO_2 level using air containing 0, 360, and 750 ppm CO_2. Four different models of FPD total sulfur analyzers were evaluated. Six or more analyzers were evaluated for each model. Supression in analyzer response due to CO_2 was observed in all four models at all three SO_2 levels.

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By proper treatment of the calibration air, the CO_2 suppression on FPD total sulfur response may be minimized. An activated charcoal scrubber is recommended for proper treatment of the calibration air.

INTRODUCTION

A recent publication by Lucero[1] reported negative interferent responses on a flame photometric detector (FPD) total sulfur analyzer from carbon dioxide (CO_2). Reports of this type on CO_2 interference resulted in the U.S. Environmental Protection Agency (EPA) conducting a special audit of several FPD total sulfur analyzers which were in use in current EPA monitoring projects. The purpose of the EPA audit was to measure the suppression in FPD total sulfur response due to CO_2 and recommend corrective action to minimize this effect.

During February and March, 1977, EPA audited 37 FPD total sulfur analyzers currently in operation in three EPA ambient air monitoring projects. The 37 analyzers represented four different manufacturers of FPD analyzers. The distribution of analyzers by manufacturer are given in Table 1. Manufacturers' models are designated as Models A, B, C, and D. None of the analyzers audited were EPA designated equivalent analyzers. All analyzers audited were purchased prior to promulgation of the EPA equivalency regulation.[2]

CO_2 EFFECT ON FPD TOTAL SULFUR MEASUREMENTS

Audit Description - Each FPD analyzer was challenged at levels of 50, 100, and 150 ppb SO_2 using air containing 0, 360, and 750 ppm CO_2. For FPD Model A, C, and D analyzers the SO_2 levels were achieved by diluting compressed gas from a cylinder containing 47.8 ppm SO_2. For the FPD Model B analyzers a National Bureau of Standards SO_2 permeation tube was used to obtain the three desired SO_2 levels. Separate cylinders of air containing 0, 360, and 750 ppm CO_2 were used to supply air to the FPD analyzers.*

Audit Results - The results from auditing the 37 FPD analyzers are shown in Tables 2, 3, 4 and 5. The effect of different levels of CO_2 in air on the total sulfur response is shown under the columns titled "Measured TS concentrations". The difference between the audit concentration and the measured total sulfur concentration (at 360 ppm CO_2) represents individual

Table 1. Summary of FPD Total Sulfur Analyzers Audited for CO_2 Effect

FPD model	Analyzers audited	Audit dates	EPA project
A	10	March 10-22, 1977	1
B	6	February 9-10, 1977	2
C	8	February 15-23, 1977	3
D	13	March 10-22, 1977	1

* Oxygen content of cylinder air analyzed at 20.8 percent.

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Table 2. CO_2 Effect on Total Sulfur Measurements - FPD Model A

Station number	Audit concentration, ppb	Measured TS concentrations			% change from 0 ppm CO_2 measurement	
		0 ppm CO_2, ppb	360 ppm CO_2, ppb	750 ppm CO_2, ppb	360 ppm CO_2	750 ppm CO_2
111	50	51	41	34	-20	-33
	99	107	92	78	-14	-27
	151	180	149	129	-17	-28
109	51	49	41	34	-16	-31
	101	111	90	74	-19	-33
	150	170	142	119	-16	-30
110	50	43	34	28	-21	-35
	100	95	76	61	-20	-36
	150	147	120	100	-18	-32
102	50	44	34	26	-23	-41
	100	98	77	61	-21	-38
	150	145	125	122	-14	-16
107	50	46	36	28	-22	-39
	100	111	84	67	-24	-40
	150	176	136	109	-23	-38
118	50	45	39	33	-13	-27
	100	101	81	66	-20	-35
	150	148	123	107	-17	-28
117	50	46	36	30	-22	-35
	100	99	78	63	-21	-36
	150	145	110	98	-24	-32
125	50	46	34	26	-26	-43
	100	116	83	62	-28	-47
	150	185	142	113	-23	-39
119	50	49	43	39	-12	-20
	100	110	93	80	-15	-27
	150	164	143	128	-13	-22
112	50	58	47	41	-19	-29
	100	124	101	87	-19	-20
	150	186	152	132	-18	-29

analyzer inaccuracy at the time of the audit.

Suppression in total sulfur analyzer response due to CO_2 was observed in all four FPD models and at all three SO_2 levels.* Not all four models, however, showed the same degree of suppression for the same SO_2 level. For example, at the 50 ppb SO_2 level, the suppression in the total sulfur responses in going from 0 to 360 ppm CO_2 were as follows: FPD Model A showed the largest suppression with an average of -19.4 percent for ten analyzers, with individual analyzers between -12 and -26 percent. Model B showed an average suppression of -6.7 percent for six analyzers, with individual analyzers between -6 and -8 percent. Model C showed an average suppression of -4.0 percent for eight analyzers, with individual analyzers between -8 and +5 percent. The lowest suppression was Model D, with an average of -1.5 percent for 13 analyzers with individual analyzers between -7 and +4 percent.

* No attempt was made during the audits to determine if the analyzers were operated in strict accordance with the manufacturers' recommendations, particularly with regard to hydrogen and sample flows.

Table 3. CO_2 Effect on Total Sulfur Measurements - FPD Model B

Station number	Audit concentration, ppb	Measured TS concentrations			% change from 0 ppm CO_2 measurement	
		0 ppm CO_2, ppb	360 ppm CO_2, ppb	750 ppm CO_2, ppb	360 ppm CO_2	750 ppm CO_2
1	59	59	55	57	-7	-3
	103	103	101	97	-2	-6
	150	150	148	144	-1	-4
2	59	53	49	44	-8	-17
	103	108	100	92	-7	-15
	150	148	142	135	-4	-9
3	59	53	50	48	-6	-9
	103	107	101	101	-6	-6
	150	149	145	140	-3	-6
4	59	51	48	46	-6	-10
	103	109	105	100	-4	-8
	150	148	146	142	-1	-4
5	59	59	55	53	-7	-10
	103	103	98	94	-5	-9
	150	150	145	139	-3	-7
6	59	52	49	46	-6	-12
	103	109	104	97	-5	-11
	150	148	145	141	-2	-5

Table 4. CO_2 Effect on Total Sulfur Measurements - FPD Model C

Station number	Audit concentration, ppb	Measured TS concentrations			% change from 0 ppm CO_2 measurement	
		0 ppm CO_2, ppb	360 ppm CO_2, ppb	750 ppm CO_2, ppb	360 ppm CO_2	750 ppm CO_2
C	50	45	46	46	+2	+2
	100	91	90	82	-1	-10
	150	138	135	114	-2	-17
J	65	61	58	53	-5	-13
	127	126	116	101	-8	-20
	188	190	174	150	-8	-21
H	50	59	54	45	-8	-24
	96	122	109	92	-11	-25
	146	192	171	149	-11	-22
M	51	48	45	41	-6	-15
	97	96	92	83	-4	-14
	150	152	142	131	-7	-14
L	51	82	76	71	-7	-13
	96	160	156	139	-3	-13
	148	261	247	226	-5	-13
T	51	49	46	41	-6	-16
	96	105	101	87	-4	-17
	148	170	157	139	-8	-18
N	51	45	42	37	-7	-18
	99	94	84	72	-11	-23
	145	150	132	113	-12	-25
K	46	41	43	41	+5	0
	87	95	94	88	-1	-7
	138	162	161	148	-1	-9

Table 5. CO_2 Effect on Total Sulfur Measurements - FPD Model D

Station number	Audit concentration, ppb	Measured TS concentrations			% change from 0 ppm CO_2 measurement	
		0 ppm CO_2, ppb	360 ppm CO_2, ppb	750 ppm CO_2, ppb	360 ppm CO_2	750 ppm CO_2
120	50	46	44	43	-4	-7
	99	95	88	84	-7	-12
	149	149	135	126	-9	-15
106	49	40	38	35	-5	-13
	102	91	87	84	-4	-8
	151	146	132	131	-10	-10
103	50	45	42	39	-7	-13
	100	95	84	78	-12	-18
	150	140	130	127	-7	-9
116	50	44	42	40	-5	-9
	99	89	81	77	-9	-13
	148	136	124	117	-9	-14
108	50	49	51	53	+4	+8
	100	105	99	99	-6	-6
	150	154	150	148	-3	-4
115	50	48	47	46	-2	-4
	100	94	88	84	-6	-11
	150	138	130	124	-6	-10
104	50	46	47	47	+2	+2
	100	101	97	94	-4	-7
	150	152	145	141	-5	-7
101	50	48	46	43	-4	-10
	101	105	97	88	-8	-16
	150	158	146	137	-8	-13
105	50	50	50	50	0	0
	100	104	100	97	-4	-7
	150	157	151	148	-4	-6
122	50	45	47	49	+4	+9
	100	102	99	100	-3	-2
	150	149	142	146	-5	-2
121	50	51	49	49	-4	-4
	100	112	106	101	-5	-10
	150	170	162	158	-5	-7
114	50	46	46	47	0	+2
	100	100	97	97	-3	-3
	150	153	153	150	0	-2
113	50	44	45	46	+2	+5
	100	99	96	94	-3	-5
	150	154	149	145	-3	-6

EVALUATION OF CALIBRATION AIR FOR CO_2 LEVEL

At all three EPA monitoring projects, ambient air is scrubbed in a clean air supply system and used as the dilution air during a multipoint calibration. Each monitoring station has a dedicated clean air supply system. The CO_2 concentration was measured simultaneously before and after these clean air supply systems with an ascarite trap* in order to determine whether CO_2 was removed by the system's scrubber. The clean air supply systems in EPA Projects 1 and 3 were selected for evaluation because each contained a different type of scrubbing adsorbent. In EPA Project 1 the ambient air passes through a molecular sieve-charcoal scrubber, and in EPA Project 3 the ambient air passes through only an activated charcoal scrubber. The CO_2 measurements in the ambient air before the

*The ascarite trap procedure used involved drawing a 3 hour sample of air at a known flow rate through a drierite drying tube followed by a preweighed ascarite trap. The gain in weight of the ascarite was used to measure the CO_2. Experimental tests established the accuracy of this method within 5 percent and a precision within 12 ppm CO_2 for duplicate measurement systems.

scrubber and in the calibration air after the scrubber are shown in Tables 6 and 7 for EPA Projects 1 and 3, respectively.

EPA Project 1 is a monitoring network in a large metropolitan area. The ambient air measurements in Table 6 represent the CO_2 levels at 23 stations within this metropolitan area. The ambient air measured between 247 and 530 ppm CO_2 and averaged 385 ppm CO_2. The calibration air resulting from this ambient air at the 23 stations measured between 6 and 173 ppm CO_2 and averaged 57 ppm CO_2. On an average for the 23 stations, the CO_2 in the calibration air was 328 ppm lower than in the ambient air. The clean air supply system consists of two molecular sieve-charcoal scrubbers with one in operation while the other one is regenerated.

Table 6. Effect of Molecular Sieve-Charcoal Scrubber on CO_2 Removal from Ambient Air - EPA Project 1

Station number	Date	Before Scrubber Ambient air CO_2, ppm	After Scrubber Calibration air CO_2, ppm
120	3/10/77	368	29
106	3/11/77	300	57
111	3/11/77	430	53
103	3/12/77	346	6
116	3/12/77	302	62
108	3/13/77	417	155
115	3/13/77	409	15
104	3/14/77	417	135
109	3/15/77	423	173
110	3/15/77	379	33
101	3/16/77	422	33
105	3/16/77	381	38
102	3/17/77	247	41
107	3/17/77	334	73
118	3/18/77	302	40
117	3/18/77	414	57
125	3/19/77	371	63
119	3/19/77	290	40
122	3/20/77	367	22
121	3/20/77	487	51
114	3/21/77	530	19
112	3/21/77	455	46
113	3/22/77	474	73

EPA Project 3 is a monitoring network around a large coal-fired power plant located in a rural area. The ambient air measurements in Table 7 represent the CO_2 levels at eight stations located around the power plant. The ambient air measurements ranged between 189 and 667 ppm CO_2. The calibration air resulting from this ambient air averaged 127 ppm CO_2 lower than the ambient air measurements. The clean air supply system consists of an activated charcoal scrubber with normal replacement of activated charcoal on a monthly basis.

The clean air supply systems containing only charcoal (EPA Project 3) resulted in much less removal of CO_2 from the ambient air compared to those systems containing regenerative molecular sieve-charcoal (EPA Project 1).

RESULTANT EFFECT ON TOTAL SULFUR MEASUREMENTS WHEN CO_2 SUPPRESSES ANALYZER RESPONSE AND CLEAN AIR SUPPLY SYSTEM REMOVES CO_2

Concern exists that some monitoring network analyzers currently in operation may be calibrated with air containing low CO_2 and then returned to service to analyze ambient air containing a significantly higher CO_2 concentration. This, of course, is only a concern if the FPD analyzers being calibrated also show a significant response to CO_2. This concern is real and can be illustrated with data collected from EPA Project 1 for the FPD Model A analyzers.

At the 50 ppb SO_2 level, the FPD Model A analyzers showed an average -19.4 percent (Table 2) suppression in the total sulfur response when the CO_2 level in the audit air was increased 360 ppm (i.e., from 0 to 360 ppm). Model A analyzers in EPA Project 1 were calibrated with air from a clean air supply system that removed a significant amount of CO_2 from the ambient air during scrubbing (Table 6). If the network of FPD Model A analyzers had all been calibrated on the audit day and had been returned immediately to service to measure total sulfur in ambient air, the CO_2 removed by the clean air supply system would have averaged 303 ppm (Table 6).* The resultant effect of an increase of 303 ppm CO_2 on the ten FPD Model A analyzers would have been a drop in the total sulfur response with an average -16.3 percent bias in the total sulfur measurements.

*FPD Model A analyzers are located in Stations 102, 107, 109, 110, 111, 112, 117, 118, 119 and 125.

Table 7. Effect of Activated Charcoal Scrubber on CO_2 Removed from Ambient Air - EPA Project 3

Station number	Date	Before Scrubber ambient air CO_2, ppm	After Scrubber calibration air CO_2, ppm
C	2/15/77	249	199
J	2/16/77	189	127
H	2/17/77	342	356
M	2/18/77	457	133
L	2/19/77	667	459
T	2/20/77	398	421
N	2/21/77	375	164
K	2/22/77	414	211

RECOMMENDED CORRECTIVE ACTION

The recommended corrective action to minimize the effect of CO_2 on an FPD total sulfur analyzer is to calibrate the analyzer with CO_2 in the calibration air that approximates the CO_2 level in sample ambient air. In a report[3] by the U.S. Environmental Protection Agency, a clean air supply system containing activated charcoal is recommended. The activated charcoal scrubs sulfur dioxide[4] from the ambient air, but allows the CO_2 to pass through the scrubber.

In addition, the air for the clean air supply system should be obtained from the station sampling manifold. Air from inside the monitoring station should not be used. The CO_2 level in air from inside the station will be higher than that in ambient air removed from the station sampling manifold.

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